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(71) Applicant(s)

Imperial Chemical Industries PLC

(Incorporated in the United Kingdom)

Imperial Chemical House, Millbank, LONDON,
SW1P 3JF, United Kingdom

(56) Documents Cited

US 4680406 A

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(72) Inventor(s)

John David Scott

James Graham Ramsbottom

(74) Agent and/or Address for Service

Alan Oldroyd

Imperial Chemical Industries PLC, ICI Group P
Patents, Group Patents Services Dept, P O Box 6,
Shire P Park, Bessemer Road, WELWYN GARDEN
CITY, Hertfordshire, AL7 1HD, United Kingdom

(54) Fluorination process

(57) A fluoro-aromatic compound, particularly a fluorobenzene, is prepared by contacting a chloro-aromatic compound, particularly a chlorobenzene, with hydrogen fluoride in the vapour phase in the presence of a zinc-promoted fluorination catalyst. A preferred catalyst is a chromium-containing catalyst such as chromia, chromium fluoride and/or chromium oxyfluoride.

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PROCESS FOR THE PRODUCTION OF FLUORO-AROMATIC
COMPOUNDS

5 This invention relates to a process for the
production of fluoro-aromatic compounds having one or
more fluorine atoms substituted on an aromatic
nucleus and particularly to a process for the
production of fluorobenzenes and
chlorofluorobenzenes.

10 Fluoro-aromatic compounds having one or more
fluorine atoms attached directly to a benzene or
other aromatic nucleus are used extensively as
intermediates in the manufacture of a variety of
agrochemicals such as herbicides and pesticides.
15 Fluorobenzenes having one or two fluorine atoms
attached directly to the benzene nucleus and which
may also have one or more chlorine atoms attached
directly to the benzene nucleus are produced on a
large scale for this purpose. However, the
20 substitution of a fluorine atom into a benzene or
other aromatic nucleus is accomplished only with
difficulty and is usually achieved by processes
involving expensive diazotisation reaction or the
formation and decomposition of fluoroformate esters.
25 These known processes employ chlorobenzenes or other
chloro-aromatic compounds as starting materials, the
chloro-aromatics, in contrast to the
fluoro-aromatics, being readily obtained by direct
chlorination procedures. Whilst direct fluorination/
30 hydrofluorination of chloro-aromatic compounds is
desirable, thereby avoiding the need for
diazotisation reactions or the formation of
fluoroformate esters, attempts to achieve this
desirable result have hitherto been unsuccessful.

35 We have now found that one or more fluorine
atoms can be introduced into aromatic compounds by

reacting chloro-aromatic compounds with hydrogen fluoride in the vapour phase over a particular type of fluorination catalyst.

5 According to the invention there is provided a process for the production of a fluoro-aromatic compound having one or more fluorine atoms substituted in the aromatic nucleus which comprises contacting a chloro-aromatic compound having one or more chlorine atoms substituted in the aromatic
10 nucleus with hydrogen fluoride in the vapour phase and in the presence of a zinc-promoted fluorination catalyst.

Whilst the process of the invention is applicable to the production of a wide range of
15 fluoro-aromatic compounds containing one or more nucleus-substituted fluorine atoms, it is particularly applicable to the production of fluoro-aromatic compounds containing a single benzene nucleus, ie fluorobenzenes and for convenience and
20 simplicity the invention is described hereinafter only in respect of the production of fluorobenzenes from chlorobenzenes. It is to be understood, however, that the invention is not limited to the production of fluorobenzenes and furthermore that the
25 process conditions (other than the catalysts) described hereinafter may not be the preferred conditions for the production of fluoro-aromatic compounds other than fluorobenzenes. The optimum process conditions (other than the catalysts) for any
30 particular fluoro-aromatic compounds can readily be determined by simple routine experiment based on the guidelines given hereinafter.

The temperature at which the chlorobenzene and hydrogen fluoride are contacted in the presence of
35 the catalyst may vary within a wide range but will

usually be from about 300°C to about 400°C. The optimum temperature may depend at least to some extent upon the particular fluorination catalyst employed but in the case of a zinc-promoted chromia catalyst the preferred temperature range is from about 320°C to about 360°C. Under these conditions the contact time will usually be from 5 seconds to 30 seconds, typically about 10 to 15 seconds.

The reaction may be carried out at atmospheric or subatmospheric pressure but will usually be under superatmospheric pressure. Pressures up to about 30 bar are suitable, preferably from about 5 bar to 15 bar.

The chlorobenzene starting materials may contain a single chlorine atom or it may contain more than one chlorine atom. Dichlorobenzenes, especially 1,3-dichlorobenzene, are preferred starting materials since replacement of one chlorine atom by a fluorine atom yields a chlorofluorobenzene which in addition to a nucleus substituted fluorine atom also contains a nucleus substituted chlorine atom to provide an active reaction site for the production of compounds useful as agrochemicals. When using dichlorobenzene as the starting material, the process conditions can be optimised to provide chlorofluorobenzene and difluorobenzene in various proportions and in particular to provide chlorofluorobenzene as the major or even essentially the sole product.

The catalyst is a zinc-promoted fluorination catalyst by which is meant a known fluorination catalyst of which the activity has been promoted or enhanced by the incorporation of zinc. Suitable catalysts, preferably chromium-containing catalysts and comprising chromia, chromium fluoride and/or chromium oxyfluoride and their production are

described in European Patent Application
No 92300563.1, Publication No 502605 A1, the
disclosure of which is incorporated herein by
reference. The amount of hydrogen fluoride will
5 usually be at least one mole per chlorine atom in the
starting material to be replaced by a fluorine atom
and generally the hydrogen fluoride will be present
in excess up to about 10 moles per mole of
chlorobenzene starting materials. If desired, the
10 hydrogen fluoride and/or the chlorobenzene starting
material may be diluted with an inert gas such as
nitrogen.

The activity of the catalyst tends to decrease
during its use and regeneration/reactivation of the
15 catalyst may be desirable. Any known catalyst
regeneration/reactivation techniques may be employed,
for example heating the used catalyst in air to burn
off carbon and organic compounds deposited on the
catalyst surface followed by treating the catalyst
20 with hydrogen fluoride to restore the activity of the
catalyst. A preferred regeneration/reactivation
technique comprises heating the used catalyst with a
mixture of air or other oxidising agent and hydrogen
fluoride, as is described in European Patent
25 Application No 91308191.5, Publication No 475693 A1,
the disclosure of which is incorporated herein by
reference.

In carrying out the process according to the
invention, the (chloro)- fluorobenzene product is
30 separated, for example by distillation and unreacted
chlorobenzene and hydrogen fluoride can be recycled.
Benzene is usually produced as a by-product and this
can be recovered from the product stream and
chlorinated to produce the chlorobenzene starting

35

material for the present process. The process may be operated continuously.

The invention is illustrated but in no way limited by the following examples.

5

EXAMPLE 1

The equipment comprised a nitrogen and HF feed system, a liquid saturator, a reactor and a batch potassium carbonate scrubbing system. The reactor comprised a $\frac{1}{2}$ " external diameter, U-tube Inconel reactor charged with 10g of catalyst of particle size 0.5-1.5 mm.

The catalyst, a zinc-promoted chromia (zinc chromite) containing 8% w/w of zinc and prepared by a technique involving co-precipitating zinc and chromium hydroxides, was charged to the U-tube reactor and the reactor was located in an oven fitted with a rapid air circulator to maintain a constant and controlled reactor temperature. The catalyst was dried with a 20 mls/minute nitrogen supply for 60 minutes. The nitrogen flow was terminated and HF was fed to the reactor at 60 mls/min to prefluorinate the catalyst at 300°C. A nitrogen flow of 100 mls/min was added to the reactor vent to avoid condensation of vapours. After 16 hours of prefluorination, the catalyst was ready for evaluation.

The monochlorobenzene feed system comprised a $\frac{1}{2}$ " diameter saturator through which was passed a 20 ml/min nitrogen flow. The chlorobenzene saturated nitrogen was then mixed with the HF feed and passed to the reactor system.

The reaction products were passed into a 2 litre batch scrubber containing potassium carbonate. After approximately one hour of operation the reactor off-gas was diverted to a sample vessel for collection and analysis.

The above sample from the reactor was injected onto a megabore DB-1 column housed in a Varian 3400 gas chromatograph operating at 40°C. The chlorobenzene conversion was found to be approximately 6.8% and the fluorobenzene yield was approximately 4.6%. A minor amount of benzene was detected in the product with traces of dihalobenzenes.

EXAMPLE 2

The equipment and general procedures were as described in Example 1.

The (62-3) zinc chromite catalyst which was used in Example 1 was cleaned of surface carbon deposits by heating for 16 hrs at 380°C in an HF:Air stream of molar ratio 20:1. The air flow was terminated and the catalyst was cooled to 300°C. Dichlorobenzene was then passed over the catalyst with the 60 mls/min of HF feed. The 1,3-dichlorobenzene was fed by passing 20 mls/min of nitrogen through a $\frac{1}{4}$ " diameter saturator. The dichlorobenzene saturated nitrogen was then mixed with the HF feed and passed to the reactor system. The reaction products were passed into a 2 litre batch scrubber containing potassium carbonate. The reaction products were sampled over a period of 65 minutes; the results are shown below. Dichlorobenzene conversion was about 23%.

In a comparative example 10g of an equivalent pure chromia catalyst was prefluorinated in HF at 300°C and fed with dichlorobenzene, as described above. The reaction products were sampled periodically and the results are shown below.

| Reaction Time (Mins) | % Yield | |
|-------------------------|--------------------------|---------------|
| | 1-chloro-3-fluorobenzene | Chlorobenzene |
| 5 | 15 | 14.1 |
| | 45 | 9.6 |
| | 65 | 10.2 |
| | | 3.3 |
| | | 2.5 |
| | | 2.5 |

Comparison

| | | | |
|----|----|-----|------|
| 10 | 15 | 0.1 | 10.3 |
| | 45 | 0.2 | 7.5 |
| | | | |

14572628

Ref. for
CLA 8-14
prior art
in
Fluorination

CLAIMS

1. A process for the production of a fluoro-aromatic compound having one or more fluorine atoms substituted in the aromatic nucleus which
5 comprises contacting a chloro-aromatic compound having one or more chlorine atoms substituted in the aromatic nucleus with hydrogen fluoride in the vapour phase and in the presence of a zinc-promoted fluorination catalyst.
- 10 2. A process as claimed in claim 1 which is carried out at a temperature in the range of 300°C to 400°C.
3. A process as claimed in claim 1 or claim 2 which is carried out under superatmospheric
15 pressure. 4. A process as claimed in claim 3 wherein the pressure is from 5 bar to 15 bar.
5. A process as claimed in any one of claims 1 to 4 wherein the catalyst is a chromium-containing catalyst.
- 20 6. A process as claimed in any one of the preceding claims wherein the amount of hydrogen fluoride is at least 1 mole per chlorine atom in the starting material to be replaced.
- 25 7. A process as claimed in claim 6 wherein the amount of hydrogen fluoride is up to 10 moles per mole of the starting material.
8. A process as claimed in any one of the preceding claims wherein the starting material is diluted with an inert gas.
- 30 9. A process as claimed in any one of the preceding claims in which unreacted starting materials are recycled.
10. A process as claimed in any one of the preceding claims wherein the starting material is a
35 chlorobenzene.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(the Search report)

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Relevant Technical Fields

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(ii) Int Cl (Ed.5) C07C 17/20

Search Examiner
P N DAVEY

Date of completion of Search
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Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI

Documents considered relevant following a search in respect of Claims :-
1-10

Categories of documents

- | | |
|--|---|
| <p>X: Document indicating lack of novelty or of inventive step.</p> <p>Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p>A: Document indicating technological background and/or state of the art.</p> | <p>P: Document published on or after the declared priority date but before the filing date of the present application.</p> <p>E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p>&: Member of the same patent family; corresponding document.</p> |
|--|---|

| Category | Identity of document and relevant passages | Relevant to claim(s) |
|----------|---|----------------------|
| X | US 4680406 (DOW) See especially column 3, line 6 - column 4, line 9 | 1-3, 5, 10 at least |

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).